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NOSC - RED PHOSPHORUS STUDY
Part I - Smoke

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U. S. NAVAL AMMUNITION DEPOT
CRANE, INDIANA



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NOSC - RED PHOSPHORUS STUDY
Part I - Smoke

by

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This report was reviewed for adequacy and technical accuracy by
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FORWARD

The red phosphorus study was funded by Naval Ordnance Systems Command (Ordtask No. Ord 332-004/060-1/UF17-546-301). This report gives the general type compositions studied under this program and draws some conclusions on the type of oxidizer to be used.

The author would also like to thank Mr. Duane M. Johnson for the helpful suggestions given during the study and to the completion of this report.

ABSTRACT

A study of red phosphorus compositions was performed using chemical and mathematical models as a means of formulation. Fluorine, chlorine, and oxygen oxidizers were studied, and the advantages and disadvantages of each are given.

The mixing of the composition was performed in solution using a precipitation and prepolymer technique. This type of mixing was used to overcome the hazard factor involved with red phosphorus compositions.

BACKGROUND

The standard red phosphorus composition is not a safe composition since numerous fires have occurred in the production mixing and pressing operation.

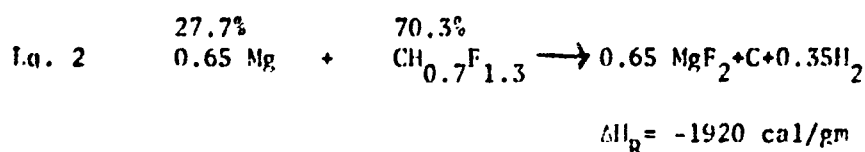
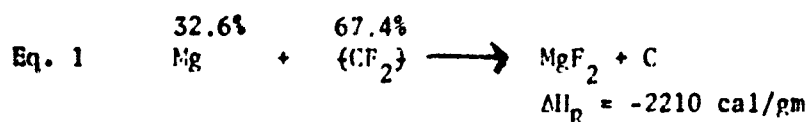
It was thought that a systematic search for new binders, fuels and oxidizers was justified in an effort to replace the standard composition. This would mean, of course, that the new composition must offer the same or slower burning rate and be safer.

Each oxidizer considered for a composition was tested for compatibility since some oxidizers form explosive mixtures with red phosphorus. To first obtain the "feel" for compatibility a mathematical treatment known as Tammann Temperature⁽¹⁾ was performed. The Tammann Temperature is the temperature at which the atoms on the surface of an oxidizer are mobile and are able to diffuse into the lattice of another compound. If the Tammann Temperature was at or below room temperature, then the oxidizer was handled very carefully in the compatibility test.

PROCEDURE OF FORMULATION

The procedure for formulating any fuel-oxidizer composition is to start with the stoichiometric ratios of the fuel and oxidizer. Assuming that the reaction goes to completion then the heat of reaction (ΔH_p) for the mixture can be calculated from known heats of formation using Hess's Law⁽²⁾.

As an example of formulation, we will be concerned with the reaction of magnesium with Teflon (Eq.1) and Viton A (Eq.2).



From the heats of vaporization for magnesium fluoride ($\Delta H_V = 1268 \text{ cal/gm}$) and red phosphorus ($\Delta H_V = 242 \text{ cal/gm}$), the magnesium fluoride will be the limiting factor in terms of calories per gram needed to melt and vaporize the products of the composition.

There are principally three unknowns, since the percent of phosphorus will depend upon what is left from the required percents of the fuel, oxidizer and binder.

To make the formulation easier it is best to set the percent binder to be used. In the example we will set the percent binder at 6 percent.

From Eq. 2 we can set up a ratio to find the percent magnesium which will be needed to react with the binder.

$$\frac{X_1\% \text{ Mg}}{29.7\% \text{ Mg}} = \frac{6\% \text{ Viton A}}{70.3\% \text{ Viton A}}$$

$$X_1\% \text{ Mg} = 2.5$$

Then using another ratio with the heat of reaction of magnesium and Viton A the heat of reaction of the binder and magnesium present in the mix can be calculated.

$$\frac{8.5\%}{X_2} = \frac{100\%}{1920 \text{ cal/gm}}$$

$$X_2 = 163 \text{ cal/gm}$$

Turning now to the major reaction of magnesium and Teflon, and the requirement that 1268 cal/gm is needed to vaporize magnesium fluoride; the percent of magnesium-Teflon can be calculated by assuming that approximately 1000 cal/gm is to be furnished by this reaction.

$$\frac{X_3\%}{1000 \text{ cal/gm}} = \frac{100\%}{2210 \text{ cal/gm}}$$

$$X_3\% = 45.3\%$$

The percents of magnesium (14.9%) and Teflon (30.4%) can be calculated from the stoichiometric reaction (Eq. 2).

The formulation can be placed into standard form of ingredients and their percent by weight in the mix.

Red Phosphorus - 46.2%

Teflon - 30.4%

Magnesium - 17.4%

Viton A - 6.0%

100%

$\Delta H_R = -1163 \text{ cal/gm}$

This heat of reaction assumes, of course, that red phosphorus is not reacting with the Teflon or Viton A. Red phosphorus does react with Teflon and Viton A, but they are endothermic reactions and will contribute nothing to the overall heat of reaction. This will be discussed further in section on Systems Studied.

PROCEDURE OF MIXING

1. Viton A and Istantane 5702

The apparatus used consisted of a small powder tank, air driven motor and a Cowles 4' blender blade.

The following procedure was used in preparing the Viton A (fluorocarbon) and Istantane (polyurethane) compositions.

1. Weigh out into powder tank the desired weight of binder (25% solution in acetone).
2. Weigh out into the powder tank the desired weight of red phosphorus.
3. Stir with rubber spatula until the phosphorus is wet (add more acetone if necessary).
4. Lower mixer blade into mix and stir until mix appears uniform.
5. Remove blade from mix and add each of the other ingredients while stirring with rubber spatula. (Add more acetone if necessary).
6. Lower mixer blade into mix and stir until mix appears uniform.
7. Add hexane very slowly until the mix is "kicked out" of the acetone (see section on Precipitation).

8. Add at least three volumes of hexane to acetone and wash for at least ten minutes.

9. Decant and add three more volumes of hexane and wash for ten minutes.

10. Decant and place mix in pan to air dry.

II. Epoxy System

The following procedure was used in preparing the epoxy bound composition.

1. Weigh out into powder tank the desired weight of red phosphorus.

2. Weigh out the desired weight of epoxy binder and dissolve with acetone.

3. Add the epoxy solution to the powder tank and stir with rubber spatula until the phosphorus is wet (add acetone if necessary).

4. Lower mixer blade into mix and stir until mix appears uniform.

5. Remove blade from mix and add each of the other ingredients while stirring with rubber spatula (add acetone if necessary).

6. Lower mixer blade into mix and stir until mix appears uniform.

7. Remove mixer blade and place mix in pan to air dry.

8. Press composition before the epoxy system sets up.

PRECIPITATION

It is necessary that the hexane be added very slowly (preferably drop-by-drop) due to local concentration effects of high polymer solutions. If the non-solvent is added slowly enough, according to Flory⁽³⁾, an equilibrium phase separation will occur. One phase will be concentrated in polymer, and the other phase will be dilute in polymer. This phase separation is termed "coacervation", and it is the point in the precipitation technique that the concentrated polymer phase is coating onto the solid particles.

It was found during this study that burning rates could be varied by varying the rate at which the non-solvent (hexane) was added to the composition. The importance of this step cannot be emphasized too strongly.

SYSTEMS STUDIED

As mentioned in section on Procedure of Formulation red phosphorus reacts with Teflon and Viton A, but the reaction is endothermic. The fluorine and chlorine oxidizers were chosen for this specific purpose. The thought being that the red phosphorus present in the mix would not contribute to the heat of reaction. Hence, the heat of reaction would depend solely on the fuel and oxidizer. This was an attempt to predict more closely the heat of reaction of the composition.

An added advantage of fluorine and chlorine oxidizers is their endothermic reaction with red phosphorus. This leaves out

any possibility of a spontaneous solid-solid reaction which might start a fire or explosion.

I. Fluorine Oxidizers

Teflon is the most fluorine oxidizer "rich" compound available. Its reaction with magnesium is sufficiently exothermic to make composition with a range from fifty to sixty percent phosphorus. Table I shows a typical composition (1), hazard data, burning rate, pressing pressure and heats of reaction. The compositions made with Teflon deteriorated over a period of time, and an odor similar to phosgene was given off. Figure I is the D. T. A. for the composition in Table I.

Other fluorine oxidizers available were much too expensive for use in pyrotechnics.

II. Chlorine Oxidizers

The chlorine oxidizers used in this investigation were hexachlorobenzene and polyvinyl chloride. These two were chosen over several others due to their stability in storage. Hexachlorobenzene and polyvinyl chloride are soluble in acetone and precipitate out after Viton A. Table I shows a typical composition (2), hazard data, burning rate, pressing pressure and heats of reaction for hexachlorobenzene. Figure II is the D. T. A. for the composition shown in Table I. Since hexachlorobenzene and polyvinyl chloride were soluble in acetone, further investigation was discontinued.

III. Oxygen Oxidizers

The principle oxygen oxidizers studied were lead dioxide and strontium nitrate. The advantages of oxygen oxidizers is easy

ignition and formation of easily vaporized products with magnesium. A typical composition of lead dioxide (3) and strontium nitrate (4) with hazard data, burning rates, pressing pressures and heats of reaction are shown in Table I. Figure III and IV are D.T.A.'s for the lead dioxide and strontium nitrate compositions.

It should be noted that boron was added to the lead dioxide to give a more even burning front.

CONCLUSIONS

From the data obtained from this study, it seems that the oxygen oxidizers offer the best possibilities for a replacement of the standard composition. The mathematical model used gives a reasonable prediction of the heat of reaction before the composition is made and gives some insight as to the calories per gram needed by the composition.

The precipitation technique has been shown to be safe to work with, and further study of precipitation techniques is in future plans.

LITERATURE CITED

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TABLE I

Composition (% weight)

	1	2	3	4
PHOSPHORUS	50	50	53	55
MAGNESIUM (GRAN 16)	16	16.8	7	
BORON			3	12
LEAD DIOXIDE			32	
STRONTIUM NITRATE				28
TEFLON #1	26			
HEXACHLOROBENZENE		25.2		
VITON A	8	8	5	
ESTANE 5702				5
ΔH (THEOR.) $\frac{\text{cal.}}{\text{gram}}$	1072	580	400	490
ΔH (EXP.) $\frac{\text{cal.}}{\text{gram}}$	903	698	359	471
IMPACT SENSITIVITY kg-cm.	50	50	46	36
FRICTION SENSITIVITY ft.-lb.	100	225	625	150
BURNING RATE $\frac{\text{sec.}}{\text{in.}}$	54	26	90	80
PRESS PRESSURE $\frac{\text{lb.}}{\text{in.}^2}$	3077	3077	3077	5385

SIZE MICRO
 REF O_2
 PROGRAM MODE Heat
 RATE 20 °, STAGE 56 °C
 ATT. U_{eq}
 T ΔT
 SCALE 100 %
 SETTING 5 %

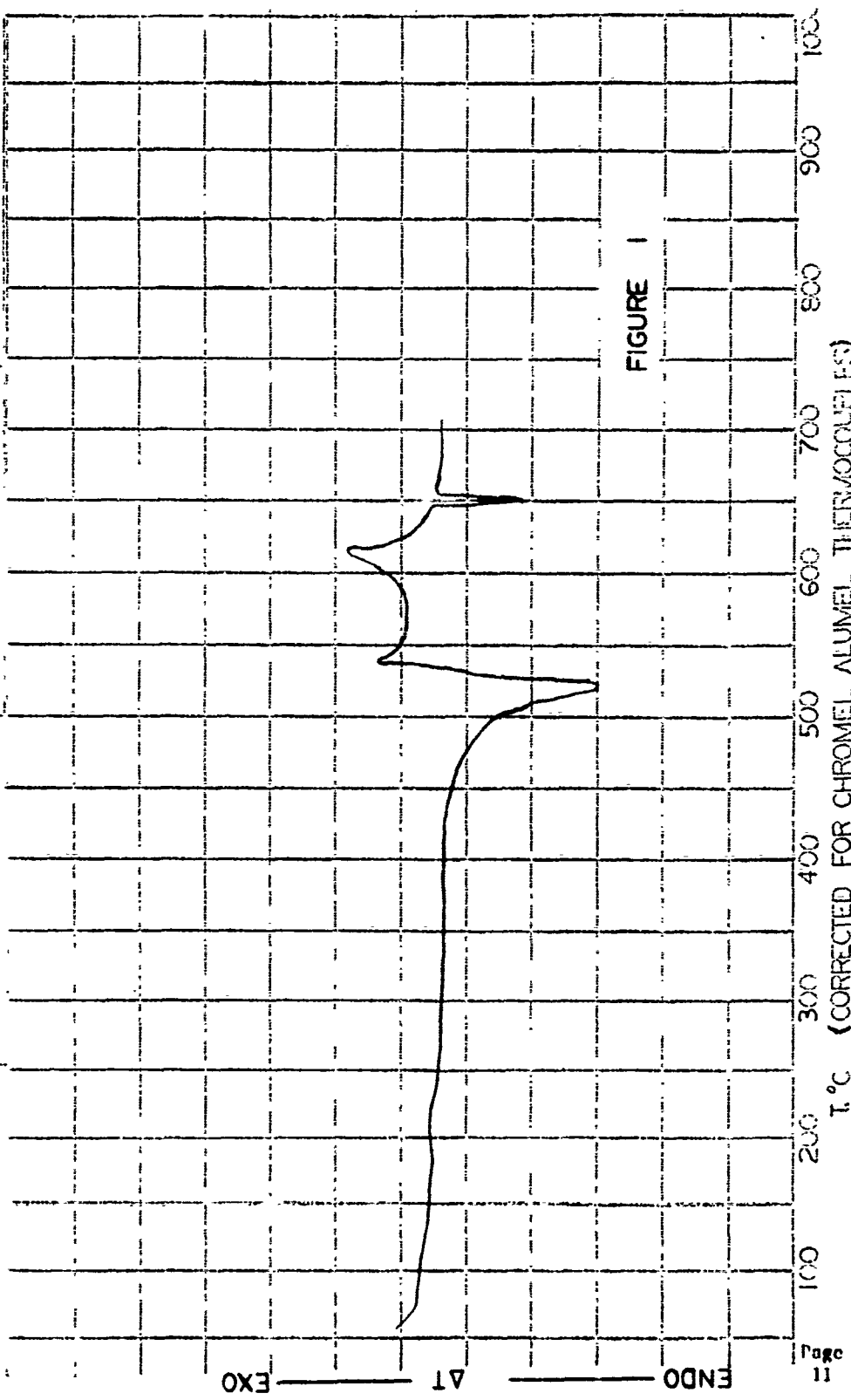


FIGURE 1

SIZE MICRO
 REF O_2, O_3
 PROGRAM MODE Heat
 RATE 5 °C, START 38 °C
 ATM. O_2
 T ΔT
 SCALE 100
 SETTING 5

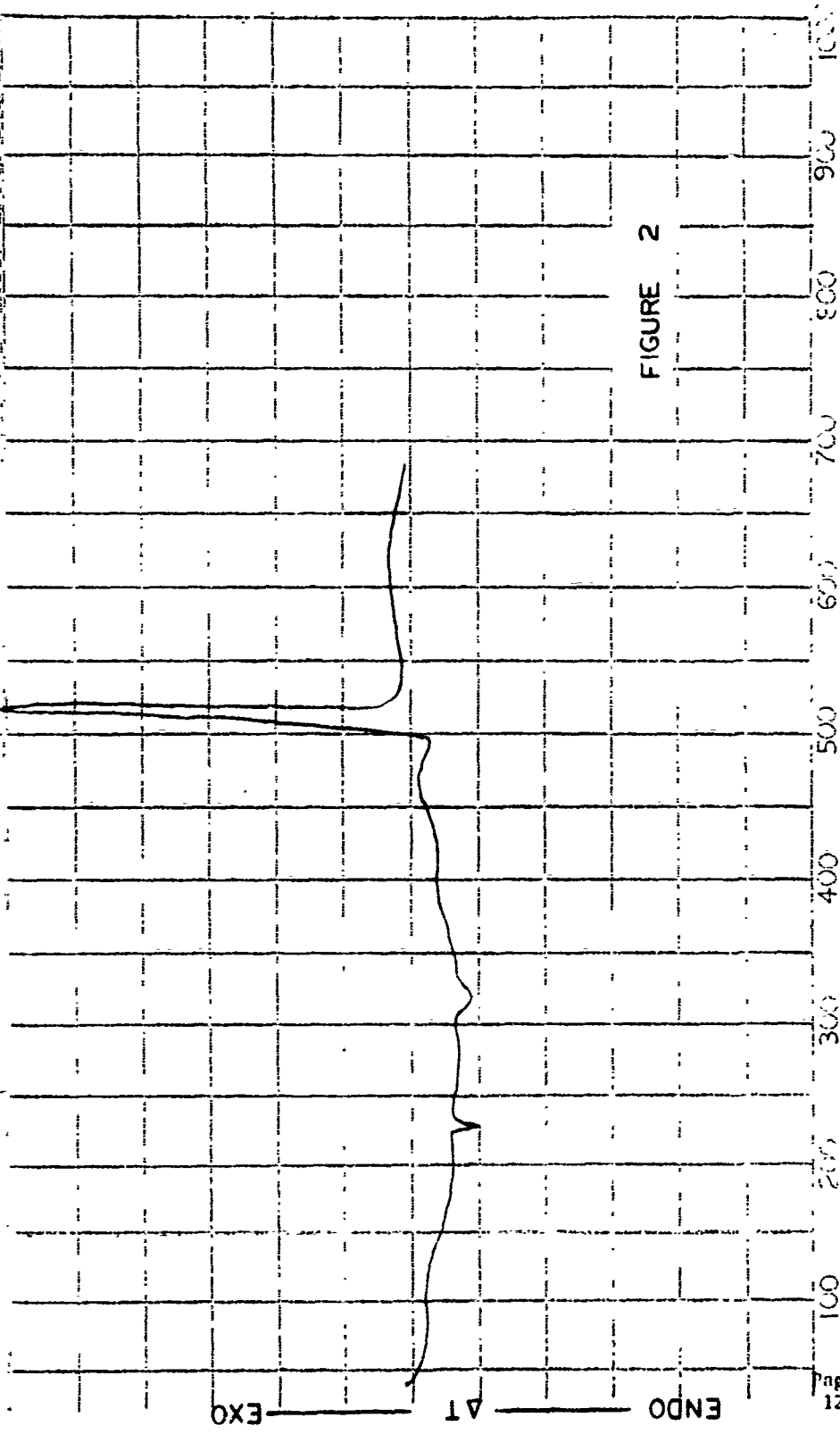


FIGURE 2

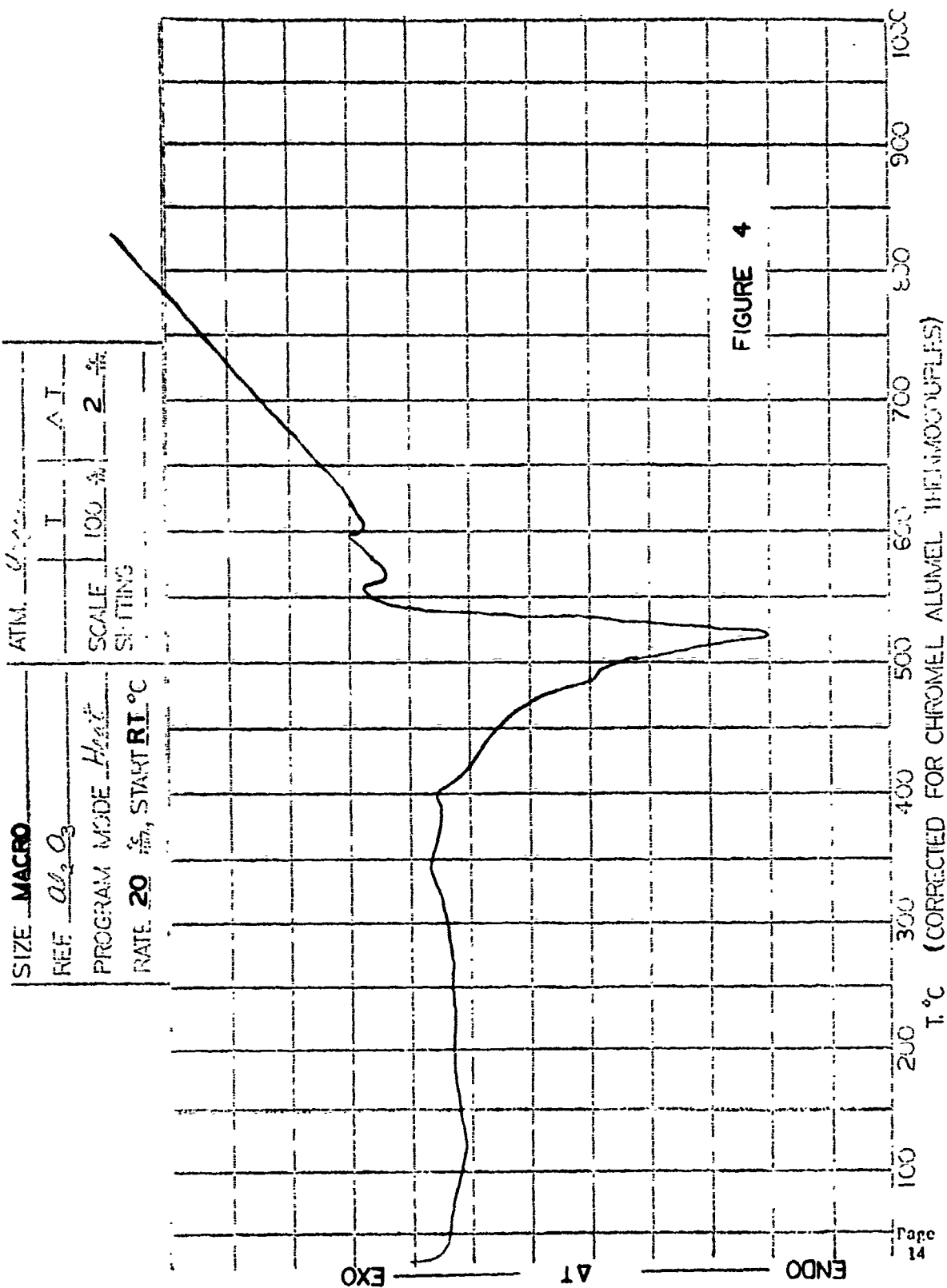
T °C (CORRECTED FOR CHROMEL ALUMEL THERMOCOUPLE)

SIZE	MACRO	ATM.	Atm.
REF	Al ₂ O ₃	T	ΔT
PROGRAM	MODE H ₂ O	SCALE	100
DATE	20. 11. 88	SETTING	2
T. °C		T. °C	



FIGURE 3

T. °C (CORRECTED FOR CHROMEL ALUMEL THERMOCOUPLES)



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